

REMARKS

In the present Action the Office has withdrawn the rejection of claims 1, 2, 7-13, 18-28, 33-39, 44-54, 59-66 and 71-80 under 35 U.S.C. §103(a) based on Mabuchi et al. (U.S. Patent No. 6,156,432) ("Mabuchi") in view of Hamada et al. (U.S. Patent No. 6,194,067) ("Hamada") that was made in the previous Action.

The Office is now rejecting claims 1, 2, 7-13, 18-28, 33-39, 44-54, 59-63, 65-66 and 71-79 under 35 U.S.C. §103(a) over Mabuchi in view of Kimihito et al. (JP 10-223223) ("Kimihito"); claims 3, 4, 14-15, 29-30, 40-41, 55-56, 64, 67-68 and 80 under 35 U.S.C. §103(a) over Mabuchi and Kimihito in view of Takami (cited in the previous Action); and claims 5, 16, 31, 42, 57 and 69 under 35 U.S.C. §103(a) over Mabuchi and Hamada in view of Tamaki (cited in the previous Action).

The position of the Office, based on the machine translation of Kimihito, is that Kimihito teaches "an outer carbon material coating having boron present" and which is provided on a first carbon material not containing boron and nitrogen. The Office alleges that a skilled artisan would find it obvious to substitute the outer coating of Kimihito for the boron nitride coating of Mabuchi to enhance the graphitization crystallinity of the "carbon

material" (coating?). (Refer to page 3 of the Action, lines 12-13).

Reconsideration and removal of the 35 U.S.C. § 103(a) rejections of the claims are respectfully requested. The machine translation of Kimihito is unclear and misleading. A complete and accurate translation of Kimihito is submitted with this response. It will be understood from the enclosed translation that Kimihito does not teach a coating of carbon which contains boron provided on another carbon material (which may or may not contain boron). No suggestion or motive is provided by Kimihito to modify Mabuchi as proposed in the Action.

Although Kimihito discloses a negative electrode material having boron present in an amount of 0.1 to 10 wt.%, it does not disclose a coating of a second carbon material containing boron on an outer surface of a first carbon material, as required in the present invention. For example, the terminology "laminated carbon net planes" seen in the abstract of the machine translation refers only to the structure of a graphitized powder of the negative electrode material, and does not describe (or remotely suggest) a coating of a second carbon material on an outer surface of a first carbon material. The abstract does not disclose an outer carbon

material coating having boron present in an amount of 0.1 to 10 wt.%.

Further, the Office also states that "the inner core layers are reasonably presumed to not contain boron and nitrogen." However, paragraph [0021] of Kimihito, the paragraph relied on by the Office as support for this presumption, discloses that "it is not so important that a part of the added catalyst is inserted between layers of the graphite crystal, or that carbon atoms forming six-membered ring network lattice in planes are replaced with said catalyst." This disclosure describes only whether a boron element is inserted into the graphite crystal lattice, and does not suggest that the inner core layers do not contain boron and nitrogen.

Kimihito, therefore, discloses only a graphitized powder having boron present in an amount of 0.1 to 10 wt.% and nitrogen present in an amount of 0.1 to 10 wt.%, and fails to disclose a coating of a second carbon material on an outer surface of a first carbon material. Mabuchi discloses only a first carbon material having an outer surface, said outer surface being coated with a second carbon material, and fails to disclose the second carbon material containing boron and nitrogen.

Therefore, no motive is provided for a person of ordinary skill in the art to have combined the Kimihito and Mabuchi references. Even if a person of ordinary skill in the art combined these references, the carbon material of the present invention, in which a second carbon material provided on a first carbon material contains 1 to 15 wt.% of boron, would not have been obtained.

The present invention discloses that the use of a carbon material in which a first carbon material is coated with a second carbon material containing 1 to 15 wt.% of boron provides a nonaqueous electrolyte secondary cell with improved storage characteristics. This result cannot reasonably be predicted from the prior art.

The foregoing is believed to be a complete and proper response to the Office Action dated October 22, 2003, and is believed to place this application in condition for allowance. If, however, minor issues remain that can be resolved by means of a telephone interview, the Examiner is respectfully requested to contact the undersigned attorney at the telephone number indicated below.

In the event that this paper is not considered to be timely filed, applicants hereby petition for an appropriate extension of time. The fee for any such extension may be charged to our Deposit Account No. 111833.

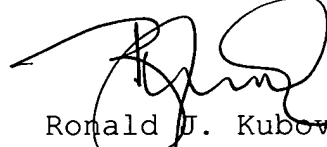
PATENT APPLN. NO. 09/576,211
RESPONSE UNDER 37 C.F.R. § 1.116

**PATENT
FINAL**

In the event any additional fees are required, please also
charge our Deposit Account No. 111833.

Respectfully submitted,

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Attachment: English translation of Kimihito et al. (JP 10-
223223)

**【Title of the Invention】**

Negative electrode material for lithium secondary cells
and process for producing the same

【Abstract】5 **【Problem to be solved】**

To provide a negative electrode material suitable for
lithium secondary cells which material has great discharge
capacity, high charge-discharge efficiency from an initial
cycle stage, excellent cycle characteristics, and

10. satisfactory load characteristics, and to provide a
production process for producing the negative electrode
material which the process is high in classification yield
of a graphitized powder, and is thus industrially excellent
in reduction of an entire production cost.

15 **【Solution】**

- A graphitized powder is prepared by heat-treating a
carbon powder made from pitch, the graphitized powder
wherein layer planes of networks of carbon atoms have the
plane spacing (d_{002}) wherein $d_{002} \leq 0.337$ nm, crystallites
20 have a size (L_c) in a c-axis direction wherein $L_c \geq 40$ nm
as determined by X-ray wide-angle diffraction method, and
boron is contained in atomic ratio of 0.1% to 10% and
nitrogen is contained in the atomic ratio of 0.1% to 10%.
The powder is produced by adding, to a carbon powder made

from pitch, a boron compound in the ratio by weight 0.1% to 25% based on boron and nitrogen compound in the ratio by weight 0.1% to 25% based on nitrogen, and mixing the resulting mixture and then heat-treating the mixture in an inert or reducing atmosphere at 2500°C or higher for 0.1 hour or longer.

【Claims】

【Claim 1】

A negative electrode material for use in lithium secondary cells which is a graphitized carbon powder being prepared by heat-treating a carbon powder made from pitch, the negative electrode material being characterized in that layer planes of networks of carbon atoms have the plane spacing (d_{002}) wherein $d_{002} \leq 0.337$ nm, crystallites have a size (L_c) in a c-axis direction wherein $L_c \geq 40$ nm as determined by X-ray wide-angle diffraction method, and boron is contained in atomic ratio of 0.1% to 10% and nitrogen is contained in the atomic ratio of 0.1% to 10%.

【Claim 2】

A production process of a negative electrode material for use in lithium secondary cells wherein 0.1 wt.% to 25 wt.% (based on boron) of a boron compound and 0.1 wt.% to 25 wt.% (based on nitrogen) of nitrogen compound are added to a carbon powder, the resulting mixture is mixed, and the

resulting powder is subject to heat treatment in an inert or reducing atmosphere at greater than 2500°C for more than 0.1 hour.

【Claim 3】

5 A production process according to claim 2 wherein the boron compound includes at least one of metallic boron, boric acid, boron oxide, boron carbide, boron nitride, and borate.

【Claim 4】

10 A production process according to claim 2 wherein the nitrogen compound includes at least one of nitride, nitrate, ammonium salt, and cyanide.

【Claim 5】

 A production process according to claim 4 wherein the
15 nitrogen compound includes boron nitride.

【Detailed Description of the Invention】

【0001】

【Technical Field to which invention belongs】

 The present invention relates to a negative electrode
20 material for use in lithium secondary cells and a process for producing the same, which utilizes insertion and elimination reaction of lithium.

【0002】

【Description of Prior Art】

Lithium secondary cells having high energy density have been mounted on portable electronic communications equipments as power sources in recent years. With the widespread market for these electronic communications equipments, the market for the lithium secondary cells are also rapidly expanded. Carbon materials are currently used as negative electrode materials for the secondary cells, and serve as a key material which influences the properties of cells. There are variations of the carbon materials having different structures, textures, and forms. This greatly makes different the properties of electrodes including an operating voltage in charging/discharging. At present, either a graphite crystalline material or an amorphous material is selected in accordance with service circumstances/conditions of the electronic equipments having mounted the cells thereon. However, the graphite crystalline materials appear to be increasingly demanded in view of the controllability of cell voltages and the energy density per cubic volume.

20 **【0003】**

Studies have long been conducted on the usage of natural graphite having an ideal graphite crystal structure (e.g., J. Electrochem. Soc., 117,222 (1970), Carbon 13,337 (1975), J-A-64-2258A, etc.). In the crystal structure,

layer planes of networks of carbon atoms are preferred-oriented to a specific direction, so that lithium in the material is diffused in limited directions, and moreover is diffused in a dramatically long distance. Accordingly it reveals that a high discharge capacity can be obtained only under an extremely small charging/discharging current (e.g., *Electrochimica Acta*, 38(9), 1179 (1993)). From a practical-use standpoint, the usage range, however, is greatly restricted since current density cannot be made high. Moreover, it has been also indicated that a mesophase spherule (meso-carbon microbead) prepared and extracted when optical anisotropy phase of mesophase pitch is generated into a spherical shape has a problem in cycle characteristics. (e.g., the 34th Cell Debate 3A07)

【0004】

A graphitization treatment at extremely high temperatures causes a pitch carbon fiber to have such spacing between layer planes of networks of carbon atoms that is approximate to the spacing of the natural graphite, as is the same as pitch coke. Moreover, lithium is diffused in various directions from a fiber periphery to interior, and is diffused in such a short distance as one half of fiber diameter from a fiber periphery to a fiber axis, i.e., about 5 μm at most, so that a powder obtained

by pulverizing the carbon fiber has a greater diffusion coefficient than the other easily-graphitized materials and is supposed to be strong against heavy loads. In fact it is recently reported that using the pitch carbon fiber provides preferable heavy load property (J. Electrochem. Soc., 142,8,2564 (1995)). On the other hand, there arise problems that even though the heat treatment is conducted at high temperatures, the crystal structure is inhibited from being developed due to the fiber being maintained form to thereby hamper the increase of discharge capacity, and that high-purification treatment of pitch and production processes of the fiberization are required for maintaining the fiber form to thereby produce higher production cost than the other materials.

15 **【0005】**

Pitch coke falls under the category of the easily-graphitized materials. By the graphitization treatment at extremely high temperatures, the pitch coke has such spacing between layer planes of networks of carbon atoms that is approximate to the spacing of the natural graphite. The graphitization of the pitch coke will not be so developed (progressed) as the natural graphite due to optical anisotropy texture of the pitch coke. As to these crystals, layer planes of networks of carbon atoms are thus

not preferred-oriented to a specific direction.

Accordingly, the pitch coke is not restricted in its usage range under high current densities unlike the natural graphite, and are therefore remarkably desirable materials

5 as the negative electrode materials for the lithium secondary cells. Therefore, a number of researches on pitch coke have ever been conducted (e.g., JP63-12257A, JP1-204361A, JP4-206276A). However, the usual coke material heat-treated at extremely high temperatures
10 (2000°C-3000°C) has lower discharge capacity (< 300 mAh/g) than the theoretical capacity (372 mAh/g), whereby further improved performance is demanded.

【0006】

Some researches on materials having structures
15 similar to those of graphite have been conducted, for example, 1) carbon powder wherein a part of carbon atom synthesized by a gas phase reaction at 900°C with vapor of boron chloride and benzene is substituted with boron, (Physical review B, Vol. 46, No. 3, 1697 (1992), JP-A-7-
20 73898 (1995)), 2) carbon powder wherein a part of carbon atom synthesized by adding a boron compound to pitch coke and giving the mixture a graphitization treatment at 2400°C is substituted with boron and nitrogen, (JP-A-5-290843 (1993)), 3) a carbon powder synthesized by adding H_3BO_3 , etc.

to pitch and giving a carbonization treatment at 1000°C
(JP-A-5-251080 (1993), JP-A-5-266880 (1993)), 4) a carbon
powder wherein a part of carbon atom synthesized by a gas
phase reaction (CVD) of pyridine is substituted with
5 nitrogen (J. Electrochem. Soc., 141,900 (1994),
Electrochemistry (Denkikagaku), 64(11), 1180 (1996)), and
etc.

【0007】

The research 1) is aimed to increase discharge
10 capacity by developing electron acceptance within the
graphite plane by substituting a part of six-membered ring
framework of carbon with boron to take in more lithium as
an electron donor. As described in the research, the
material obtained by the CVD method has the crystal
15 structure close to that of an amorphous material, and a
graphite sheet is great in spacing between the layer planes
($0.351 \text{ nm} \geq d_{002} \geq 0.337 \text{ nm}$). Moreover, crystallites are
small in size, which serve as a size index of superposed
crystals in the c-axis direction and in the a-axis
20 direction ($30 \text{ nm} > LC > 10 \text{ nm}$). Accordingly, the use of
the material is not necessarily suitable for the field of
expanding demand in the future and of demanding the
properties approximate to graphite crystalline material
since the material has extreme variations in cell voltage

for charging and discharging as in the conventional amorphous material, and the material is produced by the CVD method which is not suitable for mass production.

【0008】

5 Furthermore, the aim of the research 2) is, as in the case of 1), that compounds (BC_3 , BC_3N) are made by substituting a part of carbon forming the graphite framework with boron atom and nitrogen atom to thereby raise electron acceptance within graphite plane and to
10 improve the dope amount (discharge capacity) of lithium. Although it is unclear whether the research 3) expects that, like the cases of 1) and 2), a part of carbon atom forming the graphite framework is substituted with boron (boron substitution), or boron compounds are inserted between
15 layer planes of networks of carbon atoms (boron insertion), the boron substitution is aimed to increase the dope amount (discharge capacity) by the same mechanism as the researches 1) and 2), and the boron insertion is aimed to increase the dope amount (discharge capacity) by widening
20 spacing between the graphite layers. However, the electrical properties of the carbon powder obtained by the aforementioned 2) and 3) are generally similar to those of semiconductors, so that overvoltages during charging and discharging become great, and lithium inserted into the

carbon material cannot be efficiently extracted within a practical charging-discharging voltage range, whereby a high initial efficiency cannot be obtained. Furthermore, there are other problems, e.g., high discharge capacity cannot be obtained because the electrical properties similar to semiconductors lead to a great IR drop during charging and discharging.

【0009】

With the carbon powder obtained by the 4), like the material synthesized in the 1), the crystal structure is approximate to that of an amorphous material, a graphite sheet is great in spacing between the layer planes ($d_{002} \geq 0.337$ nm), and moreover, crystallites are extremely small in size, which serves as a size index of superposed

crystals in the c-axis direction and in the a-axis direction. Accordingly, the use of the material is not necessarily suitable for the field of expanding demand in the future and of demanding the properties approximate to graphite crystalline material because a charging-

discharging curve of the material has extreme variations in cell voltage, as are very similar to that of the conventional amorphous material, and the material is produced by the CVD method which is not suitable for mass production.

【0010】

The present inventors have intensively studied electrode properties of a variety of carbonaceous powders from the viewpoint of the crystal structure, to finally
5 find out that the higher the degree of graphitization becomes, the greater the discharge capacity is.

(Electrochemistry and Industrial physicochemistry, 61(2), 1383 (1993)) However, this series of easily graphitized carbon material obtained by the usual heat treatment up to
10 3000°C have crystal structures only developed up to less than a specified degree of graphitization, and is therefore limited in further improvement of the discharge capacity. Consequently for the further improvement of the cell performance, it is substantially most important to develop
15 a material having higher graphitization degree by a method other than the usual heat treatment at extreme high temperatures.

【0011】

The methods of obtaining carbon powders having a
20 higher graphitization degree than the carbon powders prepared by the usual heat treatment at extreme high temperatures include a method of a heat treatment under tension in the production of high-quality carbon fiber, physical methods of processing under stress of thermal

cracking carbon, etc., and a chemical method of utilizing graphitization catalyst. Among these methods, the graphitization enhancement by the graphitization catalyst improves the graphitization degree of a carbonaceous powder which is low in crystallinity by catalysis of metals and inorganic compounds.

【0012】

According to the previous investigations (e.g., Ber. Deut. Keram. Ges., 45,224 (1968)), two mechanisms are cited as the action mechanisms of the graphitization catalyst. One is a model usually called "dissolution - redeposition" mechanism wherein the catalyst dissolves a lower-degree graphitized carbonaceous material, and moves in the carbon with graphite deposited. The other is a model called "carbide formation - decomposition" mechanism wherein a lower-degree graphitized carbonaceous material reacts with the catalyst to form carbide which will decompose at a further high temperature to form graphite.

【0013】

Stated specifically, the addition of graphitization catalyst to the carbon material substantially means to enhance the development of graphite structure and texture structure in firing under coexistence of the catalyst. In firing the graphitization catalyst is solidly-solved in a

graphite crystal. This removes the distortion of the crystal, with the result that the graphite structure is developed. (Carbon, 102 (1980) 118)

【0014】

5 Studies have been conducted for many years on raising the degree of the graphitization of the carbonaceous powder by utilizing the graphitization catalyst for enhancing the graphitization. (e.g., U.S. Patent, 568323 (1896), Carbon, 41, 18 (1965), Carbon, 3,387 (1966), Carbon, 185 (1969),
10 Journal of Ceramic Society of Japan 86(12), 56 (1978), etc.) However, each of these studies is limited in focusing on the production process for cost reduction by raising the degree of graphitization at the lowest possible temperature to gain the same effect as that of the heat
15 treatment at high temperatures, or in focusing on the improvement of mechanical strength by utilizing dense form with use of the graphitization catalyst. On the other hand, the present inventors has proposed that the carbonaceous powder having improved graphitization degree by the
20 graphitization catalyst is used as a functional material in insertion-elimination reaction of lithium in the negative electrode of the lithium secondary cells (JP-A No.8-31422). However, according to said proposal made by the present inventors, nitrogen compounds are not used in the progress

of the graphitization reaction, and the electrode properties of the material proposed are not satisfactory in load characteristics under conditions similar to those in the case where the material is actually used as of the cell, 5 whereby further improvement is required. Incidentally, particles are made coarse after firing under the same condition, to thereby cause an impaired yield of end products.

【0015】

10 【Problem To Be Solved By the Invention】

An object of the present invention which has been accomplished in view of the foregoing problems is to provide a negative electrode material for lithium secondary cells which material has great discharge capacity, high 15 charge-discharge efficiency from an initial cycle, excellent cycle characteristics, and satisfactory load characteristics, and to provide a production process for producing the negative electrode material which the process is high in classification yield of a graphitization powder, 20 and is industrially excellent in reduction of an entire production cost.

【0016】

【Means For Solving the Problem】

The present inventors have intensively studied a

catalyst effect for graphitization with respect to a series of boron compounds, and consequently have found out that further addition of nitrogen compound improves the graphitized powder after firing in electrode properties, particularly in load characteristics. Furthermore in case of use of boron compound and nitrogen compound, the powder after firing is made less coarse in particle size than in case of single use of boron compound, so that a classification step after firing can be eliminated by controlling particle size before firing. This leads to a high production efficiency of end products and a simplified production step, hence an industrially excellent production process, as the present inventors have found out. The present invention is accomplished based on the foregoing findings.

【0017】

Stated specifically, the present invention provides a graphitized carbon powder being prepared by heat-treating a carbon powder made from pitch, the graphitized carbon powder being characterized in that layer planes of networks of carbon atoms have the plane spacing (d_{002}) wherein $d_{002} \leq 0.337$ nm, crystallites have a size (L_c) in a c-axis direction wherein $L_c \geq 40$ nm as determined by X-ray wide-angle diffraction method, and that boron is contained in

atomic ratio of 0.1% to 10%, and nitrogen is contained in the atomic ratio of 0.1% to 10%.

【0018】

Further, the present invention provides a production
5 process of a carbon negative electrode material for use in
lithium secondary cells wherein 0.1 wt.% to 25 wt.% (based
on boron) of a boron compound and 0.1 wt.% to 25 wt.%
(based on nitrogen) of nitrogen compound are added to a
carbon powder, the resulting mixture is mixed, and the
10 resulting powder is subject to heat treatment in an inert
or reducing atmosphere at greater than 2500°C for more than
0.1 hour.

【0019】

【Embodiment of the Invention】

15 Detailed description of the present invention will be
given below.

【0020】

According to the present invention, a carbonaceous
powder classified into the easily-graphitized carbon
20 material is heat-treated along with a boron compound and
nitrogen compound. These added compounds enhance the
graphitization of the carbon material to develop a crystal
structure of the carbon powder after the graphitization at
such a high degree that cannot be obtained by the usual

heat treatment, to thereby exhibit high discharge capacity and high initial charge-discharge efficiency, and moreover to realize excellent load characteristics owing to nitrogen present in the material. Furthermore, the physical

5 characteristics of the added compounds do not make the powder after firing coarse in particle size, whereby the invention makes it possible to produce end products with a high classification yield.

【0021】

10 An object of the present invention is to provide a carbon material made from pitch classified into easily-graphitized material which is desirable as a carbon negative electrode material for lithium secondary cells, and having a higher degree of graphitization than that

15 obtained by the usual graphitization treatment, and containing boron and nitrogen within a specified range. To achieve said object, the present invention focuses attention on the application of boron compounds and nitrogen compounds having catalytic effect for

20 graphitization. According to the present invention, it is, therefore, substantially important that the graphitization of the carbon powder is enhanced by the catalytic action for enhancing the graphitization reaction of the compounds fired with the carbon powder, whereas it is not so

important that a part of the added catalyst is inserted between layers of the graphite crystal, or that carbon atoms forming six-membered ring network lattice in planes are replaced with said catalyst.

5 **【0022】**

 The present inventors intensively studied various graphitized carbon materials, found out that structures of the materials, crystal structures, and the orientation of crystallites of material surface layers are important
10 factors, and graphitized materials utilizing catalytic effect of graphitization of boron, boron carbide, boron oxide, and boric acid exhibit extremely high electrode properties than the conventional negative electrode materials, and thereby have applied the previous invention
15 (JP-A No. 8-31422). For the present invention the present inventors study the improvement of, particularly, load characteristics of the electrode properties and the improvement of production efficiency by hampering particles from growing coarse during firing steps, and finally find
20 out that boron compounds other than the aforementioned exhibit catalytic effect of graphitization, a carbon powder given the catalytic action so as not to damage the graphitization catalytic effect of said boron compounds by adding nitrogen compounds to said boron compounds is high

in discharge capacity and in initial efficiency, and said carbon powder exhibits more excellent electrode properties in load characteristics than the system wherein each of boron, boron carbide, boron oxide, and boric acid is
5 separately added.

【0023】

The present inventors find out that the carbon powder is favorable in load characteristics which are correlated with the amount of nitrogen present in the carbon material,
10 and the presence of nitrogen is important for the improvement of load characteristics although the mechanism for the improvement has not been made clear. Furtherly found out is that the coexistence of the boron compound and the nitrogen compound hampers the powder after
15 graphitization from growing coarse in particle size with the result that end products in the range of desired particle diameters can be produced with high efficiency so as to eliminate a classification step, as is particularly remarkable when boron nitride is used as the boron compound
20 or nitrogen compound. This appears attributable to physical characteristics wherein the boron compounds other than boron nitride as of the previously applied patent have melting-points lower than the graphitization temperature ($\geq 2500^{\circ}\text{C}$) while boron nitride does not have a melting-point

and is sublimed at around 3000°C. Stated specifically, it is presumed that in the case of the boron compounds other than boron nitride, the carbon powders as the material fuse each other through catalyst-melted liquid during the firing
5 step to thereby make the powder after firing coarse in particle size, while in the case of boron nitride, the catalyst graphitization reaction progresses without the phenomenon occurring in the case of the boron compounds other than boron nitride, so that fusing and growing coarse
10 in particle size of the carbon powder as the material are unlikely to occur.

【0024】

Whereas the boron compound of the present invention is not limited as far as the boron compound contain boron,
15 the boron compound preferably include at least one of metallic boron, boric acid, boron oxide, boron carbide, boron nitride, and borate. Whereas the nitrogen compound is not limited as far as the nitrogen compounds contain nitrogen, the nitrogen compound preferably include at least
20 one of nitride, nitrate, ammonium salt, and cyanide, and more preferably boron nitride.

【0025】

It is possible to dissolve the aforementioned compounds in organic solvent like water or alcohol or

disperse the compounds in advance and thereafter to add the resulting compounds.

【0026】

With respect to the degree of graphitization serving
5 as an index of development degree of graphite structure, it
is required to satisfy $d_{002} \leq 0.337$ nm, $L_c \geq 40$ nm as a
parameter defining a carbonaceous material by X-ray
diffraction method. The carbonaceous material having said
degree of graphitization cannot be obtained except by the
10 heat treatment with use of the graphitization catalyst of
the present invention. In the case where a carbonaceous
powder is fired at temperatures of the usual heat treatment,
 $d_{002} > 0.337$ nm, and $L_c < 40$ nm are obtained, the graphite
structure is developed in low degree, lithium is small in
15 dope amount, and therefore high discharge capacity cannot
be achieved.

【0027】

The investigation on boron and nitrogen content
contained, respectively, in the graphitized carbon powder
20 after firing reveals that boron content in the material is
preferably in the range of at least 0.1% to up to 10% for
achieving excellent load characteristics while retaining
high discharge capacity and high initial efficiency. In
the case where boron content exceeds 10%, boron remains in

the graphitized material as of B_4C to the amount greater than limit amount wherein boron can be dissolved in graphite, and is, however, not involved in doping/undoping reaction of lithium to thereby reduce discharge capacity.

5 Further in the case where boron content is less than 0.1%, the added boron fails to fully fulfill its catalysis effect, so that each of the electrode properties is almost the same as that of a graphitized powder obtained by the usual heat treatment to bring about no improvement. On the other hand,
10 in the case where nitrogen content is greater than 10%, the material is increased in electric specific resistance to increase excess voltage during charging and discharging, thereby failing to increase doping/undoping amount of lithium, resulting in extreme reduction of discharge
15 capacity. In addition, mutual interaction between the doped lithium and nitrogen is intensified to increase the ratio of trapped lithium in the material, to reduce extremely initial efficiency. Further in the case where nitrogen content is less than 0.1%, load characteristics is
20 not satisfactory under the conditions similar to those in the case where the material is actually used as of the cell.

【0028】

The carbon powder made from pitch of the present invention is a material which easily forms a graphite

structure (regularity of superposed-layers arrangement of graphite layers) suitable for use as a carbon material for a negative electrode of lithium secondary cells. Included in said carbon powder are, for example, carbon fiber made
5 from pitch, pitch coke, and mesophase spherule, etc., but said carbon powder is not limited to these. Further, although restrictions are not particularly imposed on pitch as a raw material of said carbon powder, it is substantially important that said pitch is one suitable for
10 easily developing graphite crystallinity by firing, i.e., easy to be graphitized (easily-graphitized characteristics). Cited as examples for said pitch are petroleum pitch, asphalt pitch, coal tar pitch, naphthalene pitch, crude-oil-cracking pitch, petroleum sludge pitch, pitch obtained
15 by pyrolysis of macromolecule polymer, or may be one obtained by giving hydrogenation treatment to these pitches.

【0029】

According to the present invention, charge-discharge cycle properties in case of forming with a binder can be
20 raised by making the carbonaceous powder 50 μm or less in mean grain size. When the mean grain size exceeds 50 μm , it is difficult to insert lithium into the interior of the carbonaceous powder, decreasing the rate of utilization of the carbon powder, to thereby reduce discharge capacity.

Coarse grain size makes it difficult to form an electrode to be incorporated in practical use cells in uniform thickness around 100 μm , failing to fully exploit performance of the carbonaceous powder.

5 【0030】

Although restrictions are not imposed on the aforementioned pulverizing method of the carbonaceous material as far as the method is one or an apparatus for satisfying the mean grain size within the range described, 10 usable are, for example, a frictional grinding ball mill, a roller mill, a vibration disc mill of impact compression grinding type, a vibration ball mill, a pin mill, a jet mill, a stamp mill, a cutting mill of shearing grinding type, an impeller mill, etc.

15 【0031】

Boron compounds to be fired with the carbon powder made from pitch like pitch coke, i.e. boron compounds which is effective for the graphitization of the carbon powder made from pitch like pitch coke are added before firing 20 desirably in the ratio by weight of 0.1% to 25% based on boron. Extremely high temperature during firing exceeds the melting point or the boiling point of the boron compound as the graphitization catalyst, resulting in the disappearance of a part of the added boron compound during

the heat treatment. Thus boron content in the carbon powder after firing is less than the content based on boron of the boron compound added before firing. However, when the boron compound to be added before firing exceeds 25 wt.% based on boron, the boron content in the carbon powder after firing will be greater than 10% in atomic ratio, causing more boron carbide to be present as a mixture, bringing about the reduction of discharge capacity. Furthermore when the boron compound to be added is less than 0.1 wt.% based on boron, the boron compound fails to fully function as the graphitization catalyst. On the other hand, nitrogen compounds to be fired with the carbon powder made from pitch like pitch coke, i.e. nitrogen compounds which is effective for the graphitization of the carbon powder made from pitch like pitch coke are added before firing desirably in the ratio by weight of 0.1% to 25% based on nitrogen. When the nitrogen compound to be added exceeds 25 wt.% based on nitrogen, the nitrogen content in the carbon powder after firing will be greater than 10% in atomic ratio, thereby causing the reduction of initial efficiency. When the nitrogen compound to be added is less than 0.1 wt.% based on nitrogen, the nitrogen content in the carbon powder after firing will be less than 0.1% in atomic ratio, whereby load characteristics are not

satisfactory under the conditions similar to those when the material is actually used as of a cell.

【0032】

Although restrictions are not imposed on the described method of mixing the carbonaceous material with boron compounds and nitrogen compounds as far as these are mixed to homogeneity, these may be stirred up directly or be stirred up with liquid like organic solvent, e.g., water or alcohol.

10 【0033】

The temperature of the heat treatment is preferably set at the highest possible temperature in order to develop graphite crystallinity of the material after the heat treatment which is desirably conducted at 2500°C or more in an inert atmosphere (nitrogen or argon gas) or in a reducing atmosphere for 0.1 hour or more. The heat treatment at less than 2500°C does not fully develop the graphite structure of the carbon powder after graphitization, thereby rendering discharge capacity small and rendering low current efficiency especially at the first time of charge-discharge cycle. The heat treatment for less than 0.1 hour is not enough to operate catalyst effect of the graphitization catalyst, failing to develop the graphite structure of the carbonaceous powder after

firing, whereby discharge capacity and initial efficiency are not rendered high. Incidentally although the temperature of the heat treatment is desirably set at the highest possible temperature in order to advance

5 acceleration of graphitization, the temperature is preferably set at less than 3300°C because a graphitizing furnace is limited in its performance, wear and tear of equipments is accelerated with rise in temperature, the fired material is reduced in weight with rise in vapor

10 pressure of carbon in proportion to rise in temperature, and accuracy of measuring temperature becomes decreased. Furthermore in terms of hours of heat treatment, although the material is desirably fired for the longest possible period of time for operating catalyst effect of the

15 graphitization catalyst, even the heat treatment at 2500°C or more for 1000 hours or less can advance catalyst graphitization reaction to fully develop crystal structure of the carbonaceous powder, so that the heat treatment for greater than 1000 hours is not appropriate for economic

20 reason. Moreover, carbon powder as material is sintered each other due to the heat treatment for 1000 hours or more, rendering carbon particles after firing greater in grain size. This makes it impossible to efficiently obtain material within the range in grain size which is

appropriate for the production of electrodes, and therefore the heat treatment exceeding 1000 hours is not favorable.

【0034】

Restrictions are not imposed on a method or apparatus
5 for powder classification after firing as far as the method or the apparatus is one for satisfying mean grain size within the aforementioned range. To take example, screen classifiers or air classifiers can be preferably used.

【0035】

10 The graphitized carbon powder of the present invention can be formed by methods usually used for powdered cell active material for use in lithium cells, and restrictions are not imposed on the methods as far as the methods can fully exploit performance of the carbonaceous
15 powder, the methods are high in bulking characteristics to the powder, and the methods are performed in a chemically and electrochemically stable condition. The methods include one for adding, to the carbonaceous powder, powder or dispersion solution of fluorocarbon resin, such as
20 polytetrafluoroethylene and thereafter mixing and kneading the mixture. Furthermore, the methods also include another one for adding, to the carbon powder, resin powder, such as polyethylene and polyvinyl alcohol and thereafter inserting the dry mixture into metal mold to conduct formation by hot

pressing. Moreover, the methods include one for preparing a slurry obtained by mixing the carbonaceous powder using water-soluble binders, such as fluorocarbon resin powder, such as polyvinylidene fluoride, or a carboxymethyl
 5 cellulose, with solvent such as N-methyl pyrrolidone, dimethylformamide, water or alcohol, and applying the resulting slurry on a collector and dried.

【0036】

The carbon material of the present invention can be
 10 used by suitably combining positive electrode active material with organic solvent electrolyte. Restrictions are not imposed on the positive electrode active material and the organic solvent electrolyte as far as the active material and the electrolyte are usually used for lithium
 15 secondary cells.

【0037】

Usable as positive electrode active materials are, for example, lithium containing transition-metal oxide $\text{LiM}(1)_x\text{O}_2$ (x in formula is a value in the range of $0 \leq x \leq$
 20 1. M(1) in formula stands for a transition metal containing at least one of Co, Ni, Mn, Cr, Ti, V, Fe, Zn, Al, In, and Sn.), or $\text{LiM}(2)_{2-y}\text{O}_4$ (y in formula is a value in the range of $0 \leq y \leq 1$. M(2) in formula stands for a transition metal containing at least one of Co, Ni, Mn, Cr,

Ti, V, Fe, Zn, B, Al, In, and Sn.), or transition-metal chalcogenide (TiS_2 , NbSe_3 , etc.), or vanadium oxide (V_2O_5 , V_6O_{13} , V_2O_4 , and V_3O_8 , etc.) and Li compound of the vanadium oxide, or Chevrel phase compound expressed by a general
 5 formula $\text{M}_x\text{M}_{\text{O}_6}\text{Ch}_{8-y}$ (x in formula is a value in the range of $0 \leq x \leq 4$, and y in formula is a value in the range of $0 \leq y \leq 1$. M in formula stands for metals including transition-metal, and Ch stands for chalcogen element.), or activated carbon, activated carbon fiber, etc.

10 【0038】

Although restrictions are not imposed on organic solvents for use in the organic solvent electrolyte, usable as the organic solvent are one or two or more kinds of mixed solvents, such as Propylene carbonate, Ethylene
 15 carbonate, dimethyl carbonate, diethyl carbonate, 1 and 1- and 1, 2-dimethoxyethane, 1, 2-diethoxyethane, Gamma-butyrolactone, tetrahydrofuran, 2-methyl tetrahydrofuran, 1, 3-dioxolane, 4-methyl-1, 3-dioxolane, anisole, Diethylether, sulfolane, methyl sulfolane, acetonitrile, Chloro nitril,
 20 propionitrile, trimethyl borate, silicic-acid tetramethyl, Nitromethane, dimethylformamide, N-methyl pyrrolidone, ethyl acetate, trimethyl alt.formate, nitrobenzene, benzoyl chloride, benzoyl bromide, tetrahydrothiophene, dimethyl sulfoxide, 3-methyl-2-oxazolidone, ethylene glycol,

sulphite, and dimethyl sulphite.

【0039】

Usable as an electrolyte is one which is conventionally known and is a one or two or more kinds of mixtures, such as LiClO_4 , LiBF_4 , LiPF_6 , LiAsF_6 , $\text{LiB}(\text{C}_6\text{H}_5)$, LiCl , LiBr , LiCF_3SO_3 , LiCH_3SO_3 , $\text{Li}(\text{CF}_3\text{SO}_2)_2\text{N}$, $\text{Li}(\text{CF}_3\text{SO}_2)_3\text{C}$, $\text{Li}(\text{CF}_3\text{CH}_2\text{OSO}_2)_2\text{N}$, $\text{Li}(\text{CF}_3\text{CH}_2\text{CH}_2\text{OSO}_2)_2\text{N}$, $\text{Li}(\text{HCF}_2\text{CF}_2\text{CH}_2\text{OSO}_2)_2\text{N}$, $\text{Li}((\text{CF}_3)_2\text{CHOSO}_2)_2\text{N}$, $\text{LiB}(\text{C}_6\text{H}_3(\text{CF}_3)_2)_4$ etc.

【0040】

10 【Example】

Pitch coke lumps made from coal tar pitch were pulverized using a pin mill to obtain a powder having a mean grain size of 20 μm . The pitch coke powder was classified with a 75 μm screen. Then various compounds shown in Table 1 were added to the resulting powder and mixed fully, and given a graphitization treatment for an hour in an argon atmosphere, respectively. The treatment was conducted at 3000°C except the cases of the sample numbers 7, 8, wherein the treatment was conducted at 2500°C, 2700°C, respectively. Table 1 shows graphite crystal structures of the obtained graphitized powders, the amount of boron and nitrogen contained in firing powder, and classification yield with the 75 μm vibration screen. The crystal structure of the obtained graphitized powder was

approximate to the ideal graphite crystal structure ($d_{002} = 0.3354$ nm), and the graphite structure of pitch coke was developed by adding boron nitride. Furthermore the amount of nitrogen contained in the firing powder was dependent on the amount of the added boron nitride before firing. The powder after firing was measured with a grain-size-distribution measurement machine of laser diffraction scattering type, with the result that the grain-size-distribution was unchanged before and after firing. The graphitized powder was actually classified with the vibration screen, and particles within the intended range in grain size can be obtained with high efficiency.

【0041】

【Table 1】

No.	Boron compound		Nitro.compound		d_{002} (nm)	Lc (nm)	B amt. (at%)	N amt. (at%)	Class yied (%)
	compound	Amt (Bwt.%)	compound	Amt (Nwt.%)					
1	B	2	Si ₃ N ₄	2	0.3360	54	1.9	1.0	95
2	B ₂ O ₃	2	AlN	2	0.3361	56	1.7	0.8	91
3	H ₃ BO ₃	2	Ni(NO ₃) ₂	2	0.3365	42	1.6	0.7	90
4	B ₄ C	2	NaCN	2	0.3363	47	1.8	0.9	96
5	BN	2	(NH ₄) ₃ Fe (C ₂ O ₄) ₃	2	0.3361	55	1.7	0.7	93
6	Na ₂ B ₄ O ₇	2	BN	2	0.3362	49	1.8	1.9	95
7	BN	2	BN	3	0.3360	53	2.0	1.9	100
8	BN	2	BN	3	0.3358	61	2.0	1.7	100
9	BN	0.4	BN	0.6	0.3363	48	0.3	0.1	99
10	BN	2	BN	3	0.3360	55	1.8	1.2	97
11	BN	4	BN	6	0.3355	82	3.5	3.6	94
12	BN	10	BN	15	0.3354	90	8.8	9.8	90

【0042】

Polytetrafluoroethylene powder of 5 wt.% was added and kneaded as a binder to the firing powder thus prepared, to produce an electrode sheet of about 0.1 mm in thickness, to cut out the electrode sheet by about 10.5 mg (10 mg based on carbon material). Then the resulting electrode sheet was attached by pressure to Ni mesh serving as a current collector to thereby prepare a negative electrode.

【0043】

10 In order to evaluate the electrode properties of a single electrode of the aforementioned formed electrode, three-electrode type cells having a counter electrode and a reference electrode made from lithium metal were used. Used as an electrolytic solution was one prepared by
15 dissolving LiPF_6 at a rate of 1 mol/l in a mixed solvent of ethylene carbonate and diethyl carbonate (1:1 mixing in volume ratio). A charge-discharge test was conducted in constant current (0.5 mA/cm^2) for charging and discharging under potential control. The potential was in the range of
20 0V to 1.0V (based on lithium metal). With respect to the heavy load characteristic test, charging (Li absorbing) was performed in a constant current (0.5 mA/cm^2) to be charged up to 0V, and the method of constant current-constant voltage was conducted with the state of 0V retained.

Charging was performed for 12 hours in its entirety.

Discharging (Li desorbing) was performed by the method of constant current (0.5, 1, 2, 3, 4 mA/cm²), and the potential was in the range of 0V to 1.0V (based on lithium metal).

5 【0044】

 The electrode properties of the above mentioned test is shown in Table 2 and Table 3. In initial lithium dope to the carbon material, potential flat portion (plateau) approximate to 0.8V was so small that initial charge-
10 discharge efficiency was extremely high and changed to stability at almost 100% after the third cycle. The discharge capacity per weight was also high, the capacity lowering with charge-discharge cycle progress was small,
15 and excellent electrode properties were therefore exhibited. It revealed the heavy load characteristics were correlated with the amount of nitrogen contained in the firing powder, and that the more nitrogen remained, the smaller the variations of discharging capacity due to the difference of
20 current density was, whereby the electrode having more nitrogen exhibited excellent heavy load characteristics.

 【0045】

 【Table 2】

No.	Discharge capa. (mAh/g)		Charge- discharge effi. (%)		Load character.	
	1st	100th	1st	3rd	Curre.dentsity (mA/cm ²)	Discharge Capa.rate (%)
1	325	308	88	100	0.5	100
					1	100
					2	100
					4	98
2	322	306	87	100	0.5	100
					1	100
					2	99
					4	98
3	314	300	87	99	0.5	100
					1	100
					2	99
					4	97
4	319	303	89	100	0.5	100
					1	100
					2	100
					4	98
5	324	309	90	100	0.5	100
					1	100
					2	99
					4	97
6	320	304	89	100	0.5	100
					1	100
					2	100
					4	99

【0046】

【Table 3】

No.	Discharge capa. (mAh/g)		Charge- discharge effi. (%)		Load character.	
	1st	100th	1st	3rd	Curre.dentsity (mA/cm ²)	Discharge Capa.rate (%)
7	326	307	88	100	0.5	100
					1	100
					2	100
					4	98
8	337	319	89	100	0.5	100
					1	100
					2	99
					4	97
9	318	305	87	100	0.5	100
					1	100
					2	98
					4	96
10	330	318	88	100	0.5	100
					1	100
					2	100
					4	98
11	335	321	90	100	0.5	100
					1	100
					2	100
					4	99
12	325	315	88	100	0.5	100
					1	100
					2	100
					4	100

【0047】 Comparative Example 1

The same pitch coke powders as those used in the
5 above example was raised in temperature at the speed of
10°C per minute, and was subject to the graphitization
treatment at 2500°C, 2700°C, 2900°C, and 3000°C,
respectively, for an hour. Table 4 shows the graphite

crystal structure of the obtained graphitized powder, the amount of boron and nitrogen contained in the firing powder, and classification yield with the 75 μm vibration screen.

The weight before and after firing was almost unchanged

5 since a catalyst was not added. While the particles after firing were not made great in particle size, the spacing between layer planes (d_{002}) serving as an index of the graphite crystal structure was not reduced even after firing at so high temperatures.

10 【0048】

【Table 4】

No.	Fire temp. ($^{\circ}\text{C}$)	d (nm)	Lc (nm)	B amt. (at%)	N amt. (at%)	Class Yield(%)
13	2500	0.3412	21	0	0	100
14	2700	0.3388	28	0	0	100
15	2900	0.3376	31	0	0	99
16	3000	0.3373	37	0	0	99

【0049】

The pitch coke powder thus prepared was formed in the same manner of the above embodiment. The charge-discharge test was performed according to the above embodiment to show the result in Table 5. A long potential flat portion (plateau) of 0.6V to 0.9V was observed in initial lithium dope to the carbon powder, voltage difference was great
15
20 until an open-circuit state after the lithium dope, and the diffusion of lithium in the material did not easily

progress, so that charge-discharge efficiency was extremely low. Eventually, this charge-discharge reaction reached almost 100% after the fifth cycle, and thereafter transited at 100%. However the discharge capacity was low, and the capacity reduction with charge-discharge cycle was great. The load characteristics started to descend in capacity from 1 mA/cm², and, at 4 mA/cm², fell to 80% of the discharge capacity at the time of 0.5 mA/cm².

【0050】

10 【Table 5】

No.	Discharge capa. (mAh/g)		Charge-discharge effi. (%)		Load character.	
	1st	100th	1st	3rd	Curre.density (mA/cm ²)	Discharge Capa.rate (%)
13	229	205	61	97	0.5	100
					1	99
					2	95
					4	87
14	238	220	63	98	0.5	100
					1	98
					2	93
					4	85
15	251	230	65	99	0.5	100
					1	98
					2	91
					4	82
16	263	240	65	99	0.5	100
					1	96
					2	90
					4	80

【0051】 Comparative Example 2

Various boron compounds of 6 wt.% based on boron were

added and mixed, respectively, to the same pitch coke powders as those used in the above example, and the mixture was raised in temperature at the speed of 10°C per minute, and was subject to the graphitization treatment at 3000°C for an hour. Table 6 shows the graphite crystal structure of the obtained graphitized powder, the amount of boron and nitrogen contained in the firing powder, and classification yield with the 75 μm vibration screen. In any case, the spacing between layer planes (d_{002}) serving as an index of the graphite crystal structure was a value approximate to 0.3354 nm, as compared with the comparative example 1 wherein no catalyst was added in each case. On the other hand, the weight reduction before and after firing was great in the cases of adding boron oxide and boric acid. Furthermore the particles after firing of each case were made great in particle size, thereby to render the classification yield low.

【0052】

【Table 6】

No.	B compound	Fire temp. (°C)	d (nm)	Lc (nm)	B amt. (at%)	N amt. (at%)	Class Yield(%)
17	B	3000	0.3354	80	5.9	0	86
18	B ₂ O ₃	3000	0.3359	58	5.6	0	82
19	B ₄ C	3000	0.3357	68	5.8	0	87
20	H ₃ BO ₃	3000	0.3361	51	5.5	0	81

20

【0053】

The pitch coke powder thus prepared was given the same method as the above example to produce an electrode sheet, thereby preparing a negative electrode. The electrode properties of a single electrode of the

5 aforementioned formed electrode was evaluated entirely in accordance with the example. Table 7 shows the result of the electrode properties. A charge-discharge curve was almost the same as that in the case of adding boron nitride, wherein charge-discharge efficiency was high. Furthermore

10 the discharge capacity was high, the capacity reduction with charge-discharge cycle was small, and the cycle characteristics were satisfactory. On the other hand, the load characteristics started to descend in capacity from 1 mA/cm², and, at 4 mA/cm², fell to 90% of the discharge

15 capacity at 0.5 mA/cm².

【0054】

【Table 7】

No.	Discharge capa. (mAh/g)		Charge- discharge effi. (%)		Load character.	
	1st	100th	1st	3rd	Curre.dentsity (mA/cm ²)	Discharge Capa.rate (%)
17	329	315	86	100	0.5	100
					1	99
					2	96
					4	89
18	325	310	84	100	0.5	100
					1	100
					2	98
					4	91
19	321	305	85	100	0.5	100
					1	99
					2	98
					4	91
20	315	299	83	100	0.5	100
					1	99
					2	96
					4	90

【0055】

【Effect of the Invention】

5 As clarified by the above description, the present invention provides a process for producing a carbon negative electrode material for use in lithium secondary cells wherein the heat treatment was given to the carbonaceous powder classified into easily graphitized

10 carbon material, along with boron compounds and nitrogen composites serving as a graphitization catalyst. The produced material has a graphite crystal of such high degree of graphitization that cannot be obtained by the

usual heat treatment at extremely high temperatures, and is capable of having a material containing nitrogen in itself. Consequently the present invention can provide a powdered carbon material which exhibits high discharge capacity, high initial charge-discharge efficiency, and excellent load characteristics.